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# Poly(4-vinylpyridinium)hydrogen sulfate catalyzed an efficient and eco-friendly protocol for the synthesis of 9-pyrazolyl substituted-1,8-acridinediones in aqueous medium

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## ABSTRACT

A series of 9-pyrazolyl substituted-1,8-acridinediones have been prepared in a one pot procedure starting from dimedone/1,3-cyclohexanedione, 1,3-disubstituted-1*H*-pyrazole-4-carbaldehydes and ammonium acetate utilizing poly(4-vinylpyridinium)hydrogen sulfate as an efficient, eco-friendly and recyclable catalyst in aqueous medium. Analytically pure products were formed within 40-50 min in excellent yields.

## INTRODUCTION

Acridines are interesting hetero aromatic compounds that are widely studied, and exhibit broad spectrum of medicinal and biological activities such as antimicrobial [1, 2], antitumor [3], antimalarial [4] and carcinogenic activities [5]. These are also possess DNA binding, DNA photo-damaging ability [6], potassium channel blockers [7], and used as dyes and pigments [8,9]. On the other hand pyrazoles also displayed antimicrobial [10, 11], antioxidant [12], anti-inflammatory [13, 14], cytotoxic [15], antitumor [16] and antimalarial activities17].

Owing to the wide range of biological properties, many methods have been developed including traditional heating in organic solvents [18, 19], microwave irradiation method [20] and ionic liquid catalyzed reactions [21] for the preparation of substituted acridines.

In continuation of our interest on the synthesis of new heterocyclics [22-24], herein we report an efficient method for the synthesis of 9-pyrazolyl substituted-1,8-acridinediones *via* three component condensation of dimedone / 1,3-cyclohexanedione, 1,3-disubstituted-1*H* pyrazole-4-carbaldehydes and ammonium acetate utilizing poly(4-vinylpyridinium)hydrogen sulfate [P-(4-VPH)$HSO_4$] as a catalyst in aqueous medium.

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## MATERIALS AND METHODS

Melting points were determined in open capillaries using Stuart SMP30 melting point apparatus and are uncorrected. The progress of the reaction was monitored by TLC and visualized with UV light and iodine vapors. IR spectra were recorded on Perkin-Elmer 100S spectrophotometer using KBr disk. $^1$H NMR spectra were recorded on Bruker-400 MHz spectrometer using

TMS as an internal standard. The C, H and N analyses of the compounds were done on a Carlo Erba modal EA1108 and mass spectra were recorded on a Jeol JMSD-300 spectrometer.

**General procedure for the synthesis of 3,4,6,7-tetrahydro-3,3,6,6-tetramethyle-9-(1,3-disubstituted-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-diones (4a-f):**

To a mixture of dimedone (2 mmol), 1,3-disubstituted-1*H*-pyrazole-4-carbaldehyde (1 mmol) and ammonium acetate (3 mmol) in 5 mL of water, poly(4-vinylpyridinium)hydrogen sulfate (0.02 g) was added and heated at refluxing temperature for 40-50 min. Progress of the reaction was monitored by TLC, poured the contents into ice cold water. The solid thus separated out was filtered, dried and recrystallised from ethanol to afford the pure product in above 80% yield.

**General procedure for the synthesis of 3,4,6,7-Tetrahydro-9-(1,3-disubstituted-1H-pyrazol-4-yl)acridine-1,8-(2H,5H,9H,10H)-dione derivatives (6a-f):**

Poly(4-vinylpyridinium)hydrogen sulfate (0.02 g) was added to a mixture of 1,3-cyclohexanedione (2 mmol), 1,3-disubstituted-1*H*-pyrazole-4-carbaldehyde (1 mmol) and ammonium acetate (3 mmol) in 5 mL of water. The mixture was heated at refluxing temperature for 40-50 min, after completion of the reaction shown by TLC, the mixture was poured into ice cold water. Thus the solid separated out was filtered, dried and recrystallised from ethanol, furnished the pure products in above 80% yield.

**Characterization data:**

**A: 3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(1,3-diphenyl-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-dione (4a):**

Pale yellow solid; mp. 162-164 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3281, 1672, 1608, 1575, 1498, 1410, 1362; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 6H), 1.08 (s, 6H), 2.13-2.38 (m, 8H), 5.17 (s, 1H), 7.39-8.42 (m, 11H), 13.62 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 23.82, 25.91, 28.42, 31.90, 50.24, 111.82, 118.46, 126.15, 1287.34, 128.35, 129.45, 129.72, 130.26, 131.92, 138.60, 147.60, 149.32, 194.42; MS (ESI) *m/z*: 491 (M+H); Anal. Calcd. for $C_{32}H_{33}N_3O_2$: C, 78.18; H, 6.77; N, 8.55. Found: C, 78.09; H, 6.89; N, 8.48.

**B: 9-(3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-3,4,6,7-tetrahydro-3,3,6,6-tetramethyl acridine-1,8(2H,5H,9H,10H)-dione (4b):**

Pale yellow solid; mp. 148-150 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3288, 1678, 1602, 1570, 1502, 1406, 1359, 756; $^1$H NMR (400 MHz, $CDCl_3$): δ 0.98 (s, 6H), 1.05 (s, 6H), 2.09-2.25 (m, 8H), 5.18 (s, 1H), 7.19-7.23 (t, *J* = 7.6 Hz, 1H), 7.36-7.64 (m, 6H), 7.80 (s, 1H), 7.89-7.91 (d, *J* = 8.4 Hz, 2H), 13.65 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 23.85, 26.97, 28.64, 32.10, 50.22, 111.99, 117.89, 118.37, 125.84, 127.41, 127.72, 128.48, 129.32, 129.43, 129.73, 130.33, 131.89, 133.64, 139.40, 148.60, 149.35, 194.49; MS (ESI) *m/z*: 527 (M+H); Anal. Calcd. for $C_{32}H_{32}ClN_3O_2$: C, 73.06; H, 6.13; N, 7.99. Found: C, 72.97; H, 6.26; N, 7.90.

**C: 3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-dione (4c):**

Yellow solid; mp. 270-272 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3278, 1677, 1600, 1573, 1504, 1465, 1408, 1359; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 6H), 1.08 (s, 6H), 2.13-2.38 (m, 8H), 5.17(s, 1H), 7.39-7.43 (t, *J* = 7.6 Hz, 2H), 7.61-7.64 (t, *J* = 7.6 Hz, 2H), 7.69 (s, 1H), 8.34-8.36 (d, *J* = 8.8 Hz, 2H), 8.39-8.42 (d, *J* = 8.8 Hz, 2H), 13.66 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 24.05, 26.96, 28.68, 32.17, 50.17, 111.88, 118.16, 123.08, 126.27, 127.94, 129.47, 130.58, 139.27, 141.69, 136.47, 148.41, 148.77, 194.68; MS (ESI) *m/z*: 536 ($M^+$); Anal. Calcd. for $C_{32}H_{32}N_4O_4$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.76; H, 5.94; N, 10.36.

**D: 3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(1-phenyl-3-p-tolyl-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-dione (4d):**

Pale yellow solid; mp. 172-174 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3275, 1679, 1602, 1571, 1499, 1405, 1356; $^1$H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 6H), 1.01 (s, 6H), 2.00-2.17 (m, 8H), 2.38 (s, 3H), 5.23 (s, 1H), 7.17-7.38 (m, 5H), 7.62-7.66 (m, 4H), 7.89 (s, 1H), 13.68 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 20.94, 23.86, 27.07, 28.60, 32.04, 50.29, 112.00, 117.74, 125.62, 127.18, 128.23, 128.53, 129.25, 129.42, 131.90, 136.06, 139.53, 148,53, 150.60, 194.35; MS (ESI) *m/z*: 506 (M+H); Anal. Calcd. for $C_{33}H_{35}N_3O_2$: C, 78.38; H, 6.98; N, 8.31. Found: C, 78.21; H, 7.05; N, 8.28.

**E: 9-(3-Biphenyl-4-yl-1-phenyl-1H-pyrazol-4-yl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-2H,5H-acridine-1,8-dione (4e):**

Yellow solid; mp. 165-167 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3271, 1674, 1604, 1577, 1501, 1408, 1359; $^1$H NMR (400 MHz, $CDCl_3$): δ 0.97 (s, 6H), 1.03 (s, 6H), 2.02-2.19 (m, 8H), 5.13 (s, 1H), 7.17-7.81 (m, 14H), 7.87 (s, 1H), 13.68 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 24.03, 27.11, 28.58, 32.07, 50.30, 111.95, 117.84, 125.78, 125.98, 126.58, 128.99, 129.48, 138.79, 139.51, 148.65, 195.51; MS (ESI) *m/z*: 567 ($M^+$); Anal. Calcd. for $C_{38}H_{37}N_3O_2$: C, 80.39; H, 6.57; N, 7.40. Found: C, 80.48; H, 6.48; N, 7.26.

**F: 3,4,6,7-Tetrahydro-9-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)-3,3,6,6-tetramethylacridine-1,8(2H,5H,9H,10H)-dione (4f):**

White solid; mp. 218-220 °C; IR (KBr, $cm^{-1}$): 3265, 3067, 2958, 2877, 1680, 1597 1487, 1487, 1367, 1222, 1062, 995; $^1$H NMR (400 MHz, DMSO-$d_6$): δ 0.94 (s, 6H), 1.00 (s, 6H), 2.01-2.17 (m, 4H), 2.29-2.38 (m, 4H), 3.85 (s, 3H,), 5.01 (s, 1H), 7.37-7.40 (m, 1H), 7.50-7.54 (m, 2H), 7.87-7.93 (m, 2H), 7.00-7.02 (d, *J* = 7.6 Hz, 2H), 7.93-7.95 (d, *J* = 8.8 Hz, 2H), 8.13 (s, 1H), 13.51 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 23.83, 26.87, 27.62, 32.02, 50.23, 54.12, 111.72, 118.31, 125.82, 126.93, 127.52, 128.29, 129.32, 129.71, 130.32, 131.87, 133.61, 138.99, 148.64, 149.42, 194.39; MS (ESI) *m/z*: 522 (M+H); Anal. Calcd. for $C_{33}H_{35}N_3O_3$: C, 75.98; H, 6.76; N, 8.06. Found: C, 75.90; H, 6.91; N, 7.97.

**G: 3,4,6,7-Tetrahydro-9-(1,3-diphenyl-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-dione (6a):**

White solid; mp. 180-182 °C; IR (KBr, $cm^{-1}$): 3267, 3071, 1693, 1680, 1639, 1597, 1487, 1487, 995; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.60-1.64 (m, 2H), 1.74-1.78 (m, 1H), 1.90-1.95 (t, *J* = 15.6 Hz, 4H), 2.00-2.38 (m, 5H), 5.67 (s, 1H), 7.26-7.30 (t, *J* = 7.6 Hz, 1H), 7.40-7.44 (t, *J* = 7.6 Hz, 2H), 7.62 (s, 1H), 7.65-7.72 (m, 5H), 8.20-8.22 (d, *J* = 8.8 Hz, 2H), 13.61 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 22.62, 28.42, 32.10, 50.25, 111.62, 118.36, 126.15, 128.24, 129.35, 129.55, 129.82, 130.33, 121.12, 138.66, 147.73, 149.22, 194.49; MS (ESI) *m/z*: 435 ($M^+$); Anal. Calcd. for $C_{28}H_{25}N_3O_2$:C, 77.22; H, 5.79; N, 9.65. Found: C, 77.11; H, 5.86; N, 9.48.

**H: 9-(3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-3,4,6,7-tetrahydroacridine-1,8(2H,5H,9H,10H)-dione (6b):**

White solid; mp. 185-187 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3282, 1685, 1667, 1598, 1567, 1597, 761; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.49-1.52 (t, *J* = 7.2 Hz, 2H), 1.77-1.81 (d, *J* = 16.8 Hz, 2H), 1.96-1.99 (d, *J* =13.2 Hz, 2H), 2.19-2.30 (m, 6H), 5.50 (s, 1H), 7.26-7.30 (t, *J* = 7.6 Hz, 1H), 7.39-7.40 (d, *J* = 6.8 Hz, 2H), 7.46-7.50 (t, *J* = 8.0 Hz, 2H), 7.76 (s, 1H), 7.81-7.87 (t, *J* = 8.0 Hz, 4H), 13.78 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 22.85, 28.71, 32.34, 50.31, 111.89, 117.79, 119.07, 124.94, 126.91, 127.82, 128.38, 129.22, 129.32, 129.63, 130.41, 131.81, 133.72, 139.31, 148.70, 149.35, 195.01; MS (ESI) *m/z*: 470 (M+H); Anal. Calcd. for $C_{28}H_{24}ClN_3O_2$: C, 71.56; H, 5.15; N, 8.94. Found: C, 71.31; H, 5.04; N, 8.89.

**I: 3,4,6,7-Tetrahydro-9-(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-dione (6c):**

Pale yellow solid; mp. 178-180 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3269, 1693, 1677, 1600, 1573, 1504, 1465; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.61-1.65 (m, 2H), 1.75-1.79 (m, 2H), 1.91-1.96 (t, *J* = 15.6 Hz, 3H), 2.07-2.46 (m, 5H), 5.69 (s, 1H), 7.28-7.32 (t, *J* = 7.6 Hz, 1H), 7.42-7.46 (t, *J* = 8.0 Hz, 2H), 7.63 (s, 1H), 7.66-7.72 (m, 4H), 8.20-8.22 (d, *J* = 6.8 Hz, 2H), 13.62 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 22.05, 26.86, 33.01, 51.17, 111.78, 118.21, 123.12, 126.19, 127.95, 128.17, 130.52, 139.31, 142.09, 136.39, 148.43, 148.80, 194.59; MS (ESI) *m/z*: 480 ($M^+$); Anal. Calcd. for $C_{28}H_{24}N_4O_4$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.07; H, 4.98; N, 11.59.

**J: 3,4,6,7-Tetrahydro-9-(1-phenyl-3-p-tolyl-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-dione (6d):**

White solid; mp. 180-182 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3274, 1674, 1600, 1576, 1503, 1445, 1348; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.48-1.50 (t, *J* = 11.6 Hz, 2H), 1.75-1.79 (d, *J* = 16.4 Hz, 2H), 1.97-1.99 (d, *J* = 13.2 Hz, 2H), 2.19-2.30 (m, 6H), 2.38 (s, 3H), 5.52 (s, 1H), 7.22-7.28 (t, *J* = 7.6 Hz, 1H), 7.37-7.38 (d, *J* = 7.2 Hz, 2H), 7.46-7.50 (t, *J* = 7.6 Hz, 2H), 7.74 (s, 1H), 7.80-7.86 (t, *J* = 8.0 Hz, 4H), 13.76 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 20.98, 28.73, 32.12, 51.23, 112.34, 118.25, 124.92, 127.38, 128.43, 128.62, 129.35, 131.94, 136.16, 139.49, 148.43, 150.69, 194.15; MS (ESI) *m/z*: 449 ($M^+$); Anal. Calcd. for $C_{29}H_{27}N_3O_2$: C, 77.48; H, 6.05; N, 9.35. Found: C, 77.42; H, 6.11; N, 9.26.

**K: 9-(3-Biphenyl-4-yl-1-phenyl-1H-pyrazol-4-yl)-3,4,6,7,9,10-heahydro-2H,5H-acridine-1,8-dione (6e):**

Yellow solid; mp. 244-246 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3286, 1680, 1672, 1594, 1562, 1591; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.47-1.50 (t, *J* = 12.0 Hz, 2H), 1.75-1.79 (d, *J* = 16.0 Hz, 2H), 1.95-1.98 (d, *J* = 12.0 Hz, 2H), 2.19-2.30 (m, 6H), 5.53 (s, 1H), 7.24-7.26 (t, *J* = 7.6 Hz, 1H), 7.36-7.37 (d, *J* = 7.2 Hz, 2H), 7.44-7.48 (t, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.81-7.89 (m, 9H), 13.73 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 22.09, 28.68, 32.27, 50.35, 111.89, 117.88, 124.85, 126.08, 126.43, 128.73, 129.38, 138.69, 139.49, 148.60, 195.43; MS (ESI) *m/z*: 511 ($M^+$); Anal. Calcd. for $C_{34}H_{29}N_3O_2$: C, 79.82; H, 5.71; N, 8.21. Found: C, 79.92; H, 5.59; N, 7.92.

**L: 3,4,6,7-Tetrahydro-9-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)acridine 1,8(2H,5H,9H,10H)-dione (6f):**

White solid; mp. 210-212 °C; IR (KBr, $cm^{-1}$) $\upsilon_{max}$: 3268, 3062, 2948, 2867, 1685, 1592, 1479, 1222, 1069; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.64-1.67 (m, 2H), 1.76-1.78 (m, 2H), 1.90-1.95 (t, *J* = 10.4 Hz, 3H), 2.05-2.59 (m, 5H), 3.86 (s, 3H), 5.67 (s, 1H), 7.36-7.39 (m, 1H), 7.51-7.55 (m, 2H), 7.88-7.94 (m, 2H), 7.01-7.03 (d, *J* = 8.8 Hz, 2H), 7.92-7.94 (d, *J* = 8.8 Hz, 2H), 8.12 (s, 1H), 13.64 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 22.73, 28.64, 32.12, 50.13, 54.21, 111.69, 118.42, 124.84, 126.89, 127.49, 128.36, 129.38, 129.84, 130.36, 132.02, 133.58, 139.19, 148.72, 149.60, 193.19; MS (ESI) *m/z*: 465 ($M^+$); Anal. Calcd. for $C_{29}H_{27}N_3O_3$: C, 74.82; H, 5.85; N, 9.03. Found: C, 74.29; H, 5.94; N, 8.89.

## Results and Discussion

1,3-Disubstituted-1*H*-pyrazole-4-carbaldehydes **(2a-f)** were prepared according to the literature procedure [25] by double formylation of acetophenone phenylhydrazones under Vilsmeier-Haack condition. The titled compounds, 9-pyrazolyl substituted-1,8- acridinediones **(4a-f & 6a-f)** were synthesized *via* one-pot condensation of dimedone **(1)** / 1,3-cyclohexanedione **(5)** with 1,3-disubstituted-1*H*-pyrazole-4-carbaldehydes **(2a-f)** and ammonium acetate **(3)** using environmentally friendly P-(4-VPH)$HSO_4$ as a catalyst in aqueous medium.

Initially, the reaction of 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde **(2a)**, dimedone **(1)** and ammonium acetate **(3)** was carried out in aqueous medium under refluxing conditions without and with different amounts of catalyst, and observed a maximum yield of the product **(4a)** in the presence 0.02 g of catalyst. Also observed, lower amount of the catalyst resulted in low yields of the product **(4a),** while increasing the amount of catalyst beyond 0.02 g resulted no change in product yield or reaction time.

Adopting these optimistic conditions (aqueous medium, reflux, 0.02 g of catalyst), we synthesized various 9-pyrazolyl

substituted-1,8-acridinediones **(4a-f)** with splendid yield (83-93%). Under similar conditions, we have carried out the reaction with 1,3-cyclohexanedione **(5)** instead of dimedone and obtained the corresponding 1,8-acridinediones **(6a-f)** with 84-92% yields. After completion of the reaction, the catalyst was recovered by evaporating the aqueous layer, washed with acetone, dried and reused for additional five times and observed a slight decrease in its activity. For example, the reaction of 1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde **(2a)**, dimedone **(1)** and ammonium acetate **(3)** gave the corresponding 1,8-acridinedione **(4a)** in 91, 90, 88, 85 and 82% yields over extra five cycles **(Table-1, Entry-1)**. The structures of all the compounds were elucidated by IR, $^{1}$H NMR, $^{13}$C NMR and mass spectral data.

## Conclusion

We have synthesized a series of 9-pyrazolyl substituted-1,8-acridinediones *via* one-pot three component condensation of dimedone / 1,3-cyclohexanedione, 1,3-diaryl-1*H*-pyrazole-4-carbaldehydes and ammonium acetate in aqueous medium utilizing Poly(4-vinylpyridinium)hydrogen sulfate as catalyst. This method has advantages of simple work-up procedure, short reaction time, high yields and is eco-friendly.


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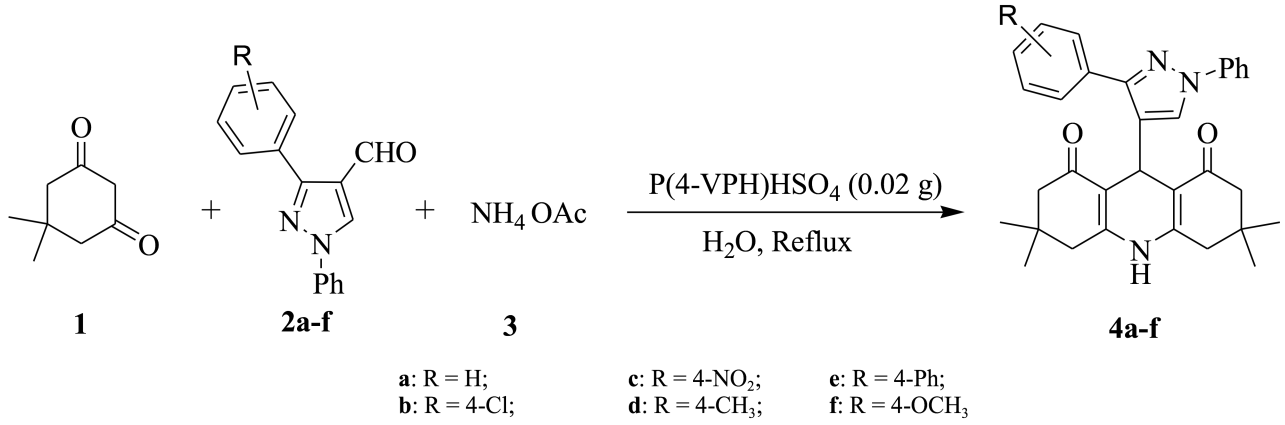
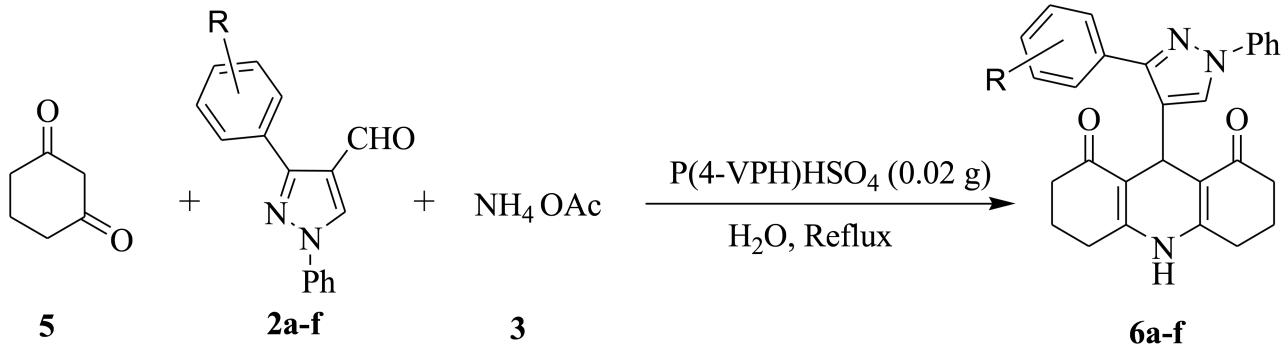



**1** **2a-f** **3** **4a-f**

**a**: R = H; **c**: R = 4-$NO_2$; **e**: R = 4-Ph;
**b**: R = 4-Cl; **d**: R = 4-$CH_3$; **f**: R = 4-$OCH_3$

**Scheme-1:** Synthesis of 3,4,6,7-tetrahydro-3,3,6,6-tetramethyle-9-(1,3-disubstituted-1H-pyrazol-4-yl)acridine-1,8(2H,5H,9H,10H)-diones.




**5** **2a-f** **3** **6a-f**

**a**: R = H; **c**: R = 4-$NO_2$; **e**: R = 4-Ph;

**b**: R = 4-Cl; **d**: R = 4-$CH_3$; **f**: R = 4-$OCH_3$

**Scheme-2:** Synthesis of 3,4,6,7-Tetrahydro-9-(1,3-disubstituted-1*H*-pyrazol-4-yl)acridine-1,8-(2*H*,5H,9*H*,10*H*)-diones.

**Table-1**: P(4-VPH)$HSO_4$ catalyzed synthesis of 9-pyrazolyl substituted-1,8-acridinediones.

| Entry[a] | R | Product | Time (min) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | H | **4a** | 50 | 92 (91,90,88,85,82)[c] |
| 2 | 4-Cl | **4b** | 45 | 89 |
| 3 | 4-$NO_2$ | **4c** | 40 | 93 |
| 4 | 4-$CH_3$ | **4d** | 50 | 91 |
| 5 | 4-Ph | **4e** | 50 | 87 |
| 6 | 4-$OCH_3$ | **4f** | 45 | 83 |
| 7 | H | **6a** | 50 | 90 |
| 8 | 4-Cl | **6b** | 45 | 92 |
| 9 | 4-$NO_2$ | **6c** | 40 | 91 |
| 10 | 4-$CH_3$ | **6d** | 45 | 88 |
| 11 | 4-Ph | **6e** | 50 | 84 |
| 12 | 4-$OCH_3$ | **6f** | 40 | 87 |

[a]**Reaction conditions**: Dimidone / 1,3-Cyclohexanedione (2 mmole), 1,3-Disubstituted-1*H*-pyrazole-4-carbaldehyde (1 mmol), Ammonium acetate (3 mmol) and Poly(4-vinylpyridinium)hydrogen sulfate (0.02 g), $H_2O$ (5 mL), reflux.

[b]Yields refer to isolated products.

[c]Yields refer to the reusability of catalyst.

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